

# PATENT SPECIFICATION

NO DRAWINGS

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844,958



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**International Classification:**—C08d.

## COMPLETE SPECIFICATION

### Rubber Compositions

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to rubber compositions.

In our copending application No. 27,133/56 (Serial No. 822,621) we describe vulcanisable compositions containing at least 50% by weight of a natural and/or synthetic rubber and less than 50% by weight of the isotactic polypropylene.

We have found that the addition of low molecular weight isotactic polypropylene to rubber stocks confers properties which render such stocks particularly suitable for extrusion and is unique in providing low density, good processing characteristics and a high degree of reinforcement.

According to the present invention, therefore, we provide a process for the production of an article comprising extruding a vulcanisable composition containing at least 50% by weight of a natural and/or synthetic rubber and less than 50% by weight of a low molecular weight isotactic polypropylene. By low molecular weight isotactic polypropylene we mean crystalline polypropylene at least 70% of which is insoluble in hot heptane and the melt viscosity of which at 190° C. is less than 10<sup>7</sup> poises when measured with a parallel plate plastometer at a shear rate of 0.1 per second.

The preferred quantity of low molecular weight isotactic polypropylene in the compositions of the process of this invention is between 5 and 20 parts per 100 parts by weight of rubber. For an optimum combination of reinforcement and extrusion properties we prefer that the isotactic polypropylene has a melt

viscosity between 10<sup>2</sup> and 10<sup>5</sup> poises at 190° C., preferably between 7 × 10<sup>3</sup> and 1 × 10<sup>5</sup> poises at 190° C. 45

Synthetic rubbers which may be used in this invention include copolymers of butadiene with styrene or acrylonitrile; copolymers of isoprene and isobutylene and polymers and copolymers of chloroprene. It will be appreciated that, if the preferred process of application No. 27,133/56 (Serial No. 822,621) is used for the production of the compositions and, if a halogen-containing rubber is used, a particularly thermally stable grade of such rubber, e.g. "Neoprene" W.R.T., should be used, as these rubbers, in general, lack thermal stability. Neoprene W.R.T. is a crystallisation-resistant grade of polychloroprene which contains no free sulphur or thiuram disulphide or other compounds capable of decomposing to give free sulphur or a vulcanisation accelerator. Further with this method of making the compositions from these rubbers, the initial compounding with isotactic polypropylene should preferably be in an internal mixer because of the lack of high temperature strength of these rubbers, e.g. on a mill, and to minimise the high temperature compounding time required. 50 55 60 65 70

The following Examples, in which all parts are by weight, serve to illustrate our invention. It will be understood, however, that our invention is in no way limited by these Examples. 75

#### EXAMPLE 1.

Compositions were prepared with and without 10 parts by weight of isotactic polypropylene, which had a melt viscosity at 190° C. of 5 × 10<sup>4</sup> poises measured on a parallel plate plastometer under a shear rate of 0.1 per second, and which when tested for solubility in heptane by Soxhlet extraction was found to be 95% by weight insoluble. The other ingredients of the compositions were:— 80 85

Ribbed smoked sheet rubber, first quality	100 parts
Sulphur	1.9 "
Semi-reinforcing furnace carbon black	25 "
Zinc oxide	2.5 "
China clay	34 "
*Surface treated precipitated calcium carbonate	40 "
Phenyl beta-naphthylamine	1.25 "
Diphenyl guanidine	0.31 "
Dibenzthiazyl disulphide	0.94 "

\* The calcium carbonate had been treated with calcium stearate (3% w/w) and was of average particle size 70—80 m/l.

In preparing these compositions the polypropylene was first milled with the rubber and phenyl beta - naphthylamine at 150° C. for 5 minutes. The sheet obtained was cooled and milled with the other ingredients on rolls heated to 60° C. In the composition containing no isotactic polypropylene the ingredients

were milled together on rolls heated to 60° C. The compositions were extruded from a 1 $\frac{1}{4}$ " rubber extruder using temperatures of 70° C. and 90° C. on the barrel and die ( $\frac{1}{4}$ " diameter) respectively and a screw speed of 40 r.p.m. with the following results:—

10

TABLE 1

	Linear output ft./hr.	Swell* ratio	Output lb./hr.	Surface Finish
Control	317	1.33	14.2	Appreciable surface rippling and imperfections
10 parts isotactic poly-propylene	654	1.14	21.9	Very smooth glossy finish

\* Swell ratio: the ratio of the diameter of the extrudate to the diameter of the die.

The compositions were also cured by pressing for 20 minutes at 141° C. and tested in accordance with British Standard Specifica-

tion 903 (1950) as amended, was the following results:—

20

TABLE 2

	Modulus at 100% strain p.s.i.	Modulus at 200% strain p.s.i.	Modulus at 300% strain p.s.i.	Tensile Strength p.s.i.	Elongation at break %
Control (no poly- propylene)	337	740	1260	2220	453
10 parts isotactic poly- propylene	560	1020	1600	2100	380

## EXAMPLES 2—6.

- In these examples the compositions were prepared by banding the rubber, and the anti-oxidant when used as shown below, or an open roll mill at 160° C., the polypropylene being added slowly with continuous knifing until dispersion was complete. The stock was then removed to a warm mill at a temperature around 5 70—80° C. and rolled for 2 minutes with cooling water directed to both rolls. The other ingredients of the mix were then added in the usual way. In control compositions containing 10

no isotactic polypropylene the ingredients were milled together on rolls heated to 60° C. 15

Extrusion properties were assessed using a 1½" rubber extruder with temperatures of 70° C. and 90° C. on the barrel and die (4" diameter) respectively and a screw speed of 40 r.p.m. 20

Vulcanisation conditions were as indicated below and mechanical properties of the compositions were tested in accordance with British Standard Specification 903 (1950) as amended. 25

The isotactic polypropylenes used were:

Isotactic  
Polypropylene A Melt Viscosity at 190° C.,  $1 \times 10^4$  poises

" B " " " "  $4 \times 10^3$  "

- The melt viscosities of these isotactic polypropylenes were measured on a parallel plate plastometer under a shear rate of 0.1 per second. These isotactic polypropylenes, when tested for solubility in heptane by Soxhlet ex-

traction, were found to be 95% by weight insoluble.

A control composition was prepared using the following ingredients:— 35

Ribbed smoked sheet, first quality	100	parts
Sulphur	1.9	"
Semi-reinforcing furnace carbon black	25	"
Zinc oxide	2.5	"
China clay	34	"
*Surface treated precipitated calcium carbonate	40	"
Phenyl beta-naphthylamine	1.25	"
Diphenyl guanidine	0.31	"
Dibenzthiazyl disulphide	0.94	"

In the examples the rubber contained added isotactic polypropylene milled into it as described.

\* (As in Example I)

TABLE 3

Example	Compound	Linear Output (ft./hr.)	Swell* Ratio	Output (lbs./hr.)	Surface Finish
	Control	317	1.33	14.2	Surface rippling and imperfections
2	10 parts by weight weight isotactic polypropylene A	720	1.18	25.8	Smooth, glossy
3	10 parts by weight isotactic poly- propylene B	760	1.20	29.5	

\* Swell ratio: the ratio of the diameter of the extrudate to the diameter of the die.

After vulcanising for 30 minutes at 153° C. the mechanical properties of these compositions were found to be:

TABLE 4

Example	Compound	Modulus at 100% strain p.s.i.	Modulus at 300% strain p.s.i.	Tensile Strength p.s.i.	Elongation at break %
	Control	340	1260	2220	450
2	10 parts by weight isotactic poly- propylene A	520	1500	2050	400
3	10 parts by weight isotactic poly- propylene B	400	1400	1750	380

The same procedure was applied using GR-S rubber and the following basic vulcanisable composition:

75% Butadiene/25% Styrene copolymer (GR-S rubber)	100 parts
Stearic acid	3.5 ,,
Sulphur	1.65 ,,
Zinc oxide	5 ,,
Easy processing channel black	42 ,,
Coumarone resin	5 ,,
Mercaptobenzthiazole	1.25 ,,
Diphenyl guanidine	0.1. ,,

Extrusion results with GR-S compositions were:—

TABLE 5

Example	Compound	Linear Output (ft./hr.)	Swell* Ratio	Output (lbs./hr.)	Surface Finish
4	Control	336	1.72	24.4	Surface rippling
	5 parts by weight isotactic poly-propylene A	436	1.63	26.5	Smooth

\* Swell ratio: the ratio of the diameter of the extrudate to the diameter of the die.

The mechanical tests on these GR-S compositions after vulcanising for 25 minutes at 153° C. showed:

TABLE 6

Example	Compound	Modulus at 100% strain p.s.i.	Modulus at 300% strain p.s.i.	Tensile Strength p.s.i.	Elongation at break %	Hardness °B.S.*
4	Control	210	580	2280	720	57
	5 parts by weight isotactic poly-propylene A	260	980	2760	560	67

\* °B.S. = degrees British Standard Hardness. (B.S. 903 (1950))

With butyl rubber the following basic vulcanisable composition was used with the same testing procedure:

95% Isobutylene/5% Isoprene copolymer (Butyl Rubber)	100 parts
Medium processing channel black	20 "
Semi-reinforcing furance black	30 "
Zinc oxide	5 "
Petroleum jelly	3 "
Tetramethyl thiuram disulphide	1 "
Zinc diethyl dithiocarbamate	1.5 "
Sulphur	2.5 "

Extrusion results with butyl rubber compositions were:

TABLE 7

Example	Compound	Linear Output (ft./hr.)	Swell* Ratio	Output (lbs./hr.)	Surface Finish
	Control	478	1.42	28.5	Surface rippling
5	10 parts by weight isotactic poly-propylene A	570	1.20	29.0	Smooth

\* Swell ratio: the ratio of the diameter of the extrudate to the diameter of the die.

The mechanical tests on these butyl rubber compositions after vulcanising for 15 minutes at 153° C. showed:

TABLE 8

Example	Compound	Modulus at 100% strain p.s.i.	Modulus at 300% strain p.s.i.	Tensile Strength p.s.i.	Elongation at break %	Hardness °B.S.*
	Control	125	280	1860	890	60
5	10 parts by weight isotactic poly-propylene A	240	840	1780	540	75

\* "B.S. = degrees British Standard Hardness.

With nitrile rubber the following basic vulcanisable composition was used with the same testing procedure, except that the coumarone resin of the control composition was omitted when polypropylene was added.

67% Butadiene/33% Acrylonitrile copolymer (Nitrile Rubber)	100 parts
Fast extrusion furnace black	50 "
Thermatomic black	70 "
Coumarone resin	20 "
Dibutyl phthalate	15 "
Paraffin wax	4 "
Antioxidant consisting of a condensate of diphenylamine and acetone	1 "
Zinc oxide	5 "
Dibenthiazyl disulphide	1.2 "
Sulphur	2 "

Extrusion results with nitrile rubber compositions were:

TABLE 9

Example	Compound	Linear Output (ft./hr.)	Swell* Ratio	Output (lbs./hr.)	Surface Finish
6	Control	642	1.27	29.6	Smooth
	20 parts by weight isotactic polypropylene A	612	1.16	21.8	Glossy

\* Swell ratio: the ratio of the diameter of the extrudate to the diameter of the die.

The mechanical tests on these nitrile rubber compositions after vulcanising for 35 minutes at 153° C. showed:

TABLE 10

Example	Compound	Modulus at 100% strain p.s.i.	Modulus at 300% strain p.s.i.	Tensile Strength p.s.i.	Elongation at break %	Hardness °B.S.*
6	Control	410	1680	2020	370	65
	20 parts by weight isotactic polypropylene A	880	1880	2070	360	83

\* °B.S. = degrees British Standard Hardness.

**WHAT WE CLAIM IS:—**

1. A process for the production of an article comprising extruding a vulcanisable composition containing at least 50% by weight of a natural or synthetic rubber and less than 50% by weight of low molecular weight isotactic polypropylene.
- 5 2. A process as claimed in Claim 1 in which the quantity of isotactic polypropylene in the said composition is between 5 and 20 parts per 100 parts by weight of rubber.
- 10 3. A process as claimed in either Claim 1 or Claim 2 in which the isotactic polypropylene has a melt viscosity between  $10^2$  and  $10^5$  poises at  $190^\circ$  C.
- 15 4. A process as claimed in any of the preceding claims in which the isotactic polypropylene has a melt viscosity between  $7 \times 10^1$  and  $1 \times 10^5$  poises at  $190^\circ$  C.
5. A process of extruding a composition of rubber and isotactic polypropylene substantially as described, particularly with reference to Example 1.
- 20 6. A process of extruding a composition of rubber and isotactic polypropylene substantially as described with reference to Examples 2—6.

ALFRED O. BALL,  
Agent for the Applicants.

**PROVISIONAL SPECIFICATION****Rubber Compositions**

We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, of Imperial Chemical House, Millbank, London, S.W.1, a British Company, do hereby declare this invention to be described in the following statement:—

This invention relates to rubber compositions. In our copending application No. 27,133/56 (Serial No. 822,621) we describe vulcanisable compositions containing a major proportion of natural and/or synthetic rubber and a lesser proportion of isotactic polypropylene. We have found that the addition of low molecular weight isotactic polypropylene to rubber stocks confers properties which render such stocks particularly suitable for extrusion and is unique in providing low density, good processing characteristics and a high degree of reinforcement.

According to the present invention, therefore we provide a process of extruding a composition containing a major proportion of natural and/or synthetic rubber and a lesser proportion of low molecular weight isotactic polypropylene. By low molecular weight isotactic polypropylene we mean crystalline polypropylene at least 70% of which is insoluble in hot heptane and the melt viscosity of which is insoluble in hot heptane and the melt viscosity of which at  $190^\circ$  C. is less than  $10^7$  poises when measured with a parallel plate plasto-

meter at a shear rate of 0.1 per second.

Synthetic rubbers which may be used in this invention include copolymers of butadiene, styrene or acrylonitrile, copolymers of isoprene and isobutylene, and polymers and copolymers of chloroprene.

The preferred quantity of low molecular weight isotactic polypropylene in the compositions of the process of this invention is between 5 and 20 parts per 100 parts by weight of rubber. For an optimum combination of reinforcement and extrusion properties we prefer that the isotactic polypropylene has a melt viscosity between  $10^2$  and  $10^5$  poises at  $190^\circ$  C.

The following Example, in which all parts are by weight, serves to illustrate our invention. It will be understood, however, that our invention is in no way limited by this Example.

**EXAMPLE.**

Compositions were prepared with and without 10 parts by weight of isotactic polypropylene, which had a melt viscosity at  $190^\circ$  C. of  $5 \times 10^1$  poises measured on a parallel plate plastometer under a shear rate of 0.1 per second, and which when tested for solubility in heptane by Soxhlet extraction was found to be 95% by weight insoluble. The other ingredients of the compositions were:—

Ribbed smoked sheet rubber, first quality	100 parts
Sulphur	1.9 "
Semi-reinforcing furnace carbon black	25 "
Zinc oxide	2.5 "
China clay	34 "
Surface treated precipitated calcium carbonate	40 "
Phenyl beta-naphthylamine	1.25 "
Diphenyl guanidine	.31 "
Dibenzthiazyl disulphide	.94 "

5 In preparing these compositions the polypropylene was first milled with the rubber and phenyl beta - naphthylamine at 150° C. for 5 minutes. The sheet obtained was cooled and milled with the other ingredients on rolls heated to 60° C. In the composition containing no isotactic polypropylene the ingredients

were milled together on rolls heated to 60° C. The compositions were extruded from a 1 $\frac{1}{4}$ " rubber extruder using temperatures of 70° C. and 90° C. on the barrel and die ( $\frac{1}{4}$ " diameter) respectively and a screw speed of 40 r.p.m. with the following results: —

15

	Linear output ft./hr.	Swell* ratio	Output lb./hr.	Surface Finish
Control	317	1.33	14.2	Appreciable surface rippling and imperfections
10 parts isotactic poly-propylene	654	1.14	21.9	Very smooth glossy finish

\* Swell ratio : the ratio of the diameter of the extrudate to the diameter of the die.

The compositions were also cured by pressing for 20 minutes at 141° C. and tested in accordance with British Standards Specification 903 (1950) as amended, with the following results:—

	Modulus at 100% strain p.s.i.	Modulus at 200% strain p.s.i.	Modulus at 300% strain p.s.i.	Tensile Strength p.s.i.	Elongation %
Control (no poly- propylene)	337	740	1260	2220	453
10 parts isotactic poly- propylene	560	1020	1600	2100	380

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